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<b>(54) Title:</b> ADHESIVE AND ENCAPSULATING MATERIAL WITH FLUXING PROPERTIES  <b>(57) Abstract</b>  Use is made in attachment of an electrical component to an electrical termination on a component-carrying substrate by a solder bump technique of a thermally curable adhesive composition for encapsulating purposes which comprises a thermosetting polymer and a chemical cross-linking agent which has fluxing properties but which is unreactive or of severely restricted reactivity with the polymer without the action of heat and/or catalyst. The composition is to be thermally curable when heated to soldering temperatures in a reaction which is catalysable merely by metal oxide fluxed from metal surfaces by cross-linking agent then dissolved in the thermosetting polymer.		

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ADHESIVE AND ENCAPSULATING MATERIAL  
WITH FLUXING PROPERTIES

5           This invention relates to electrical  
interconnection methods in electronic circuitry and  
more particularly to flip chip attachment and  
encapsulation of both naked semi-conductors and chip  
scale packages (CSPs). The technology is commonly  
10 referred to as underfill technology.

As is noted in US-A-5 128 746, solder bump  
interconnections when attaching chips to electronic  
circuitry eliminate the expense, performance  
limitations, low productivity and poor space  
15 utilisation of wire bonding. As circuit density  
increases occur, while circuit board and assembly sizes  
continue to shrink, so-called flip-chip interconnection  
using solder bumps has proved to be the most suitable  
technique for satisfying such demands.

20           With the most common form of flip-chip  
interconnection, solder bumps are placed on terminals  
of the integrated circuit being produced while the  
substrate for the integrated circuit is still in the  
form of a small wafer or die. Commonly, the eutectic  
25 Sn/Pb 60/40 or a high melting point alloy such as Sn/Pb  
3/97, which is known to have been employed in the IBM  
C4 process, is employed as solder material. The die or  
wafer carrying the integrated circuit is to be joined  
to a substrate and for this purpose the die or wafer  
30 will be inverted (hence the term flip-chip). It is  
current manufacturing practice to place a flux or  
solder paste on the substrate. This material will  
promote the adhesion of the die to the substrate during  
reflow of the solder bump. During reflow, the assembly  
35 produced is subjected to a temperature sufficient to  
melt or collapse (C4 process) the solder bump and form

the required interconnections. The flux residue must then be removed to prevent corrosion occurring to the die and, importantly, to allow free ingress of a subsequent underfill resin which is to encapsulate the various semi-conductors of the electronic circuitry produced.

For this latter purpose, an underfill encapsulant resin is applied around and under the die following reflow and flux removal. The very small gap between the die and substrate must be completely filled in order to provide environmental protection for the device. The filling of this gap is dependent on capillary action of the encapsulant material between the integrated circuit and substrate. The filling of the gap has proved to be a procedure which is very time consuming, expensive and difficult to achieve in the desired quality and is generally an unreliable procedure, particularly when a relatively large die is used. Moreover, the low viscosity of encapsulant material needed to ensure capillary action runs counter to the need to control thermal expansion and thermal conductivity by filling the encapsulation resin with ceramic powder which generally increases the viscosity of the resin. A solution to this problem has been to heat the substrate/component assembly to reduce initially the viscosity of the underfilling encapsulant resin. Temperatures must be precisely controlled and the process is difficult to control since the elevated temperature triggers the curing mechanism thus raising viscosity prematurely. For these various reasons, the underfilling process currently employed has low productivity and high space/equipment needs.

In the aforementioned US-A-5 128 746, it is proposed to add a fluxing agent to a cross-linking agent - containing encapsulant resin, the encapsulant resin being dispensed onto the substrate before the

integrated circuit-carrying chip is placed in the encapsulant resin for reflow. US-A-5 128 746 discloses the use of certain strong organic dicarboxylic acids as examples of commercially available fluxing agents. A  
5 fluxing encapsulant resin of such type has three very serious drawbacks which compromise the integrity of the interconnection. Free acid remains in the encapsulant after reflow and can and will attack and corrode metal present, especially on the die or wafer. This problem  
10 is exacerbated by the decreased environmental resistance of such adhesive composition due to the presence of unreacted resin. As the adhesive composition has relatively low resistance to humidity and moisture, the corrosion problem is thus  
15 intensified. Moreover, the addition of acids of the stated type to epoxy resin adhesives compromises the stability of the adhesive, greatly reducing pot life and making cure characteristics variable. This will have a major effect on reliability and process control.

20 Finally, it is known that salts formed during fluxing of materials by reaction between metal oxides and fluxing agent and containing various metals including tin and lead can have a catalytic action on polymer materials thus causing a premature cure of the  
25 polymer prior to reflow of the solder.

It is an object of this invention to provide a thoroughly curable adhesive which does not suffer the problem of unreacted acid remaining in the encapsulant after reflow or the problem of pre-cure of the polymer  
30 due to salts formed during fluxing.

According to one aspect of the present invention there is provided a thermally curable adhesive composition which comprises:

- 35 (a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to

the action of a chemical crosslinking agent;  
(b) a chemical crosslinking agent for said  
polymer, the crosslinking agent having fluxing  
properties and exhibiting no reactivity, or  
5 exhibiting very restricted reactivity with the  
polymer without the action of a catalyst and/or of  
heat; and

which composition is thermally curable when heated to  
soldering temperatures in the presence of a catalyst  
10 for the crosslinking of the polymer with a crosslinking  
agent and is storage and reaction stable in the absence  
of such catalyst and at ambient temperatures.

A crosslinking agent to be employed in the  
practice of the present invention will have fluxing  
15 properties so as to enable it to remove oxides from the  
material with which it is in contact, i.e. die and  
substrate metallisation and, more particularly, solder  
metal, thereby allowing solder joint formation. The  
crosslinking agent, when present in sufficient amount,  
20 is to be capable of complete reaction with  
thermosetting polymer to neutralise, i.e. react with  
all reaction sites of the polymer. The design of the  
adhesive is preferably intended to ensure absence of  
residual cross-linking agent therein and hence  
25 equimolar quantities of polymer and crosslinking agent  
are generally used. However, excess cross-linking  
agent is not a problem in the practice of this  
invention. Although it has the potential to corrode  
metal surfaces which are normally accessible via  
30 pinholes which are present unavoidably in resin, now  
any excess cross-linking agent remains trapped in the  
polymer matrix together with catalyst so that corrosion  
of metal is not a problem. The composition itself is  
storage and reaction stable until heated to a  
35 temperature at which the latent reaction catalyst  
effectively causes the crosslinking agent to cure the

thermosetting polymer and at which temperature the crosslinking agent will have melted and dissolved in the polymer or monomer.

Thus, the present invention provides chip  
5 underfill and encapsulation adhesive compositions having fluxing properties which enable one to achieve overall a rugged structure with protection of integrated circuits which have been previously solder bumped and then flip chip connected to a substrate with  
10 a metallisation pattern. During reflow, the fluxing achieved with the crosslinking agent allows metallic interconnection to be achieved between solder bump and metallisation pads on the substrate. The adhesive composition then reacts and cures to provide a fully  
15 adhered encapsulate underfill that is non-corrosive and environmentally resistant. The adhesive compositions themselves are stable and provide a long storage life at ambient temperatures, typically 20-25°C, while maintaining predictable processing characteristics.  
20 The adhesive compositions lack the substantial debilitating defects in the hitherto known compositions by providing a means for predepositing the underfill and eliminating separate fluxing and cleaning. The adhesive composition may be modified to optimise CTE,  
25 glass transition temperature ( $T_g$ ), elasticity modulus and thermal conductivity without detriment to the aforementioned benefits or detriment to the require rheological properties which allow for ease of deposition, for example by syringe dispensing. In  
30 addition, curing is achieved readily during any suitable thermal treatment, for example during reflow soldering. The underfill may only be partially cured after one or several solder reflow cycles, thus enabling ease of reworking of the device. Full cure is  
35 then achieved in a separate post-cure heat application. Alternatively, full cure may be obtained from one or

two reflow cycles if reworkability is not required.

The invention thus also provides, in a second aspect, a method of producing an electronic device which comprises opposing an electrical component having a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive composition according to the first aspect of the invention being applied to a metal surface at one and/or both of said electrical component and said substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced from said monomer or polymer in situ, catalysis of crosslinking of the thermally curable adhesive being achieved by metal oxide removed from metal surfaces by the fluxing composition and/or salts formed by reaction between metal oxide and crosslinking agent.

Insofar as the solder is concerned, this may consist of one or more metals which provide a suitable low melting point material. The metals employed are typically selected from tin, lead, bismuth, cadmium, zinc, gallium, indium, tellurium, mercury, thallium, antimony and selenium. The preferred such metal is tin or a tin/lead alloy. Specific examples of solders which may be employed are the aforementioned eutectic Sn/Pb 60/40 and the high melting point Sn/Pb 3/97.

The thermosetting polymer or monomer utilised in the compositions of this invention is an adhesive substance which is preferably liquid at ambient temperature. Thus one may utilise a reactive polyester or an epoxide monomer or polymer such as an epoxy



Novolak or epoxide precursor thereof. A preferred epoxy resin is either a diglycidyl ether of bisphenol A or a diglycidyl ether of bisphenol F. In preferred practice, such an epoxy resin is a B-stage resin or a resin which may be "B-staged" after application, thereby making it possible for there to be a delay before bringing together the component and the substrate. Other preferred epoxy materials to use are substances from the Araldite series of Ciba-Geigy Resins, such as the trifunctional epoxide MY10510 and the difunctional cycloaliphatic epoxide ERL 4221 which may be used singly or in admixture. The Araldite MY10510 may be replaced by Aradite MY9512, a tetra-functional epoxide. MY9512 may be used alone, too, as may the trifunctional epoxide MY10510. The composition of the invention may also contain a monomer precursor for a polymer, e.g. an epoxide compound when an epoxy resin is required. Mixtures of such epoxy materials may also be used.

The crosslinking agent with fluxing properties is usually solid at ambient temperature, but, provided it meets the reactivity requirements set out above for crosslinking agents of adhesive composition embodying this invention, it can also be liquid at ambient temperatures. The crosslinking agent is preferably a di-or polycarboxyl compound which is unreactive at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperatures, and such cross linking agents are generally referred to hereafter as polyacids. The cross-linking agent is preferably solid for this reason. Such polyacids serve as a fluxing agent for the oxide material present on the solder, which metal oxide is a catalyst for reaction between an epoxy resin and the carboxyl groups of the polymer at elevated temperatures. Such polyacid may be in particular a

carboxylated polymer, a multifunctional polyanhydride or a long chain ( $C_8$  or greater, preferably  $C_{10}$  or greater) polycarboxylic acid, preferably dicarboxylic acid. These acidic reactive compounds having a  
5 functionality greater than 1 provide multiple reaction sites, with epoxy resin serving to create a macromolecule that provides adhesion. A particularly preferred example of a polymer containing two or more carboxyl groups which may be employed is a styrene-  
10 acrylic acid copolymer. A preferred dicarboxylic acid is dodecanedioic acid (DDDA).

The polyanhydrides which may be used as cross-linking agent with fluxing properties in the practice of this invention and which are preferably solid  
15 include polyazelaic polyanhydride and polyadipic polyanhydride. These materials provide stability when and mixed with epoxy resin and become active fluxing and curing agents only when heated to their melting points.

20 Other crosslinking agents with fluxing properties which can be used are mono, di- and polyhydrazides which are solid at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperature. A preferred such compound is  
25 adipic dihydrazide. Because of the differing reactivities of polycarboxylic acids and hydrazides, it is preferred to use a mixture of crosslinking agents, such as dodecanedioic acid and adipic dihydrazide, the higher reactivity of the latter being countered by the  
30 lower reactivity of the former.

While the oxide removed from the solder or a salt produced by reaction between the polyacid and such oxide, as a result of the fluxing activity of the crosslinking agent, acts as a catalyst for the curing  
35 of the polymer, curing in the manner of a snap cure fix is achieved only when a catalyst is present, such

catalyst being active at the elevated temperature utilised for soldering. A preferred such latent catalyst is an imidazole catalyst especially phenyl imidazole. This effect is often not desirable as it is  
5 contrary to the need to adjust positioning of components during soldering. Other latent reaction catalysts which can be used are tertiary amines with the amine groups optionally substituting the reactive monomer or polymer, as in the aforesaid Araldite  
10 MY10510 or MY9512, or metallic salts such as tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

Preferred compositions embodying the invention will have a thermosetting polymer-crosslinking  
15 agent/flux content in which there are from 45 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 55 to 30% by weight, more preferably 50 to 40%, by weight crosslinking agent/flux.

These curing agents may be combined so as to  
20 produce a range of products which provide underfill rigidity ranging from

The use in adhesive compositions employed for encapsulating flip chip connections of ceramic powders to enhance thermal expansion and modulus properties of  
25 the composition has already been mentioned herein and is preferably to be adopted in the practice of the present invention. It is preferred that such ceramic powders be highly thermally conductive to enhance the connection between solder bump and conductor on the  
30 substrate while ensuring that the compositions retain the low viscosity necessary for fluxing and for ease of deposition. The filler is preferably a nominally  $5\mu$  diameter spherical ceramic bead or hollow sphere composition. More generally, it maybe a glass or  
35 ceramic powder comprising spherical particles of 0.1- $25\mu$ , preferably 1- $15\mu$ , diameter or comprise essentially

monodisperse spherical particles having a single diameter of  $0.1\text{-}25\mu$ , preferably  $1\text{-}15\mu$ . The ceramic powder has preferably a very high thermal conductivity. Examples of such ceramic powders which may be employed are  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2/\text{ZnO}$ , barium sulphate and diamond dust. In some cases, it is preferred that the ceramic powder utilised has instead a very low or negative coefficient of thermal expansion, too, and if this requirement is imposed on the ceramic powder then a preferred example is aluminium lithium silicate.

Metal oxides formed on solder metals even at ambient temperatures are themselves a problem since they can catalyse crosslinking of the thermosetting resin or its monomer precursor. In accordance with a preferred embodiment of the invention, the resin or precursor contains an acid flux which is liquid at temperatures below  $100^\circ\text{C}$ , preferably below  $40^\circ\text{C}$ , more preferably ambient temperature. This acid will react with oxides to form salts which will not decompose until at elevated temperatures, in particular soldering temperatures when the resulting oxides, together with oxides formed on the metal surfaces more readily at the higher temperatures and removed from the metal surfaces by the flux/crosslinking agent, will catalyse the crosslinking of the thermosetting polymer.

The term "acid" as such is used herein to denote the more volatile flux for preventing prepolymerisation/crosslinking and to distinguish it from the solid crosslinking agent/flux. The more volatile flux is generally liquid at ambient temperature so that it acts immediately as a flux. It should certainly be liquid, at least at temperatures below those at which the crosslinking agents used become fully reactive in the presence of metal oxide/salt crosslinking catalysts. It is thus preferred that the acid used for preventing

prepolymerisation, even if solid at ambient temperature, is liquid by 40°C.

Such liquid acids may be polyacids, but will normally be monocarboxylic acids. The acids preferably contain at least 8 carbon atoms and are exemplified by versatic acids, in particular versatic 10 which is a synthetic acid composed of a mixture of highly branched isomers of C<sub>n</sub> monocarboxylic acids, mainly of tertiary structure. The high degree of branching gives rise to steric hindrance which means that the salts formed are thoroughly stable and difficult to break down. Other acids which may be used are capric acid, caprylic lauric acid, stearic acid and palmitic acid.

When such monocarboxylic acids are to be used, compositions embodying the invention preferably will have a thermosetting polymer - flux content in which there are 30 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 70 to 30%, more preferably 50 to 40%, by weight of a mixture of fluxes, the flux components consisting of from 80 to 97%, preferably 85 to 95%, by weight of solid crosslinking agent/flux and from 20 to 3%, preferably 15 to 5%, by weight of acid flux which is liquid at below 100°C.

When utilising the compositions of the invention, there is no need for them to be introduced subsequent to formation of a solder connection with the attendant difficulties identified above. It is possible for the composition to be predeposited, before emplacement and soldering of electronic component to substrate, on either or both of the electronic component and the substrate. As there is no need for a separate fluxing agent to be employed which is not incorporated in the adhesive composition, the presence of the composition on one or other of the electronic component and the substrate fulfils the required fluxing function.

Insofar as the composition may be applied to the electronic component, then this may be to the die overall whether it is in wafer form or as separate discrete devices. Application of the composition may  
5 be by screen printing, stencil printing, dispensing, spinning or any other known method for applying a composition to discrete areas.

The ease of working in accordance with the method of this invention enables the composition to contain  
10 the thermosetting resin in the form of a B-stageable precursor for application to die, substrate or carrier tape and then B-staging so as to form a handleable film which becomes fully crosslinked only when the soldering operation is carried out.

15 The following examples illustrate the adhesive compositions which may be used in the practice of this invention. In the examples all percentages are percentages by weight.

Example 1

20	ERL 4221	40.6%
	MY9512	12.7%
	DDDA	46.7%

This composition was functionally good and of satisfactory viscosity for most applications.

25

Example 2

	ERL 4221	39.65%
	Epoxy MY9512	12.40%
	DDDA	41.05%
30	Versatic 10	6.90%

This composition was functionally good in not undergoing pre-crosslinking but had too low a viscosity for some applications. As a result, higher viscosity compositions as follows were made up and found to work  
35 well.

Example 3

	ERL 4221	33.45%
	MY9512	18.60%
	DDDA	41.05%
5	Versatic 10	6.90%

Example 4

	ERL 4221	26.05%
	MY9512	26.00%
10	DDDA	41.05%
	Versatic 10	6.90%

Example 5

	ERL 4221	12.40%
15	MY9512	39.65%
	DDDA	41.05%
	Versatic 10	6.90%

The initial viscosity of the composition is here somewhat too high for ease of use. Moreover, while Examples 2 to 5 made use of monocarboxylic acids liquid at ambient temperature, it is also possible to use monocarboxylic acids solid at ambient temperature but liquid at temperatures below those at which the crosslinking agent/flux are, for example, as follows:-

25

Example 6

	ERL 4221	39.65%
	Epoxy MY9512	12.40%
	DDDA	41.05%
30	Prifrac2960	6.90% (C16 Palmitic acid - solid metals at 60°C)

Example 7

	ERL 4221	39.65%
35	Epoxy MY9512	12.40%
	DDDA	41.05%

Versatic 10 6.90% (C18 - melts at 69°C)

Finally compositions were formulated which  
contained lower amounts of monocarboxylic acid. These,  
5 too, proved to be satisfactory.

Example 8

	ERL 4221	39.65%
	MY9512	12.40%
10	DDDA	44.95%
	Versatic 10	3.00%

Example 9

	ERL 4221	42.62%
15	MY9512	13.33%
	DDDA	41.05%
	Versatic 10	3.00%



CLAIMS

1. A thermally curable adhesive composition which comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent;

(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

which composition is thermally curable when heated to soldering temperatures in the presence of a catalyst for the crosslinking of the polymer with a crosslinking agent and is storage and reaction stable in the absence of such catalyst and at ambient temperatures.

2. A composition according to claim 1, wherein the chemical crosslinking agent is solid at ambient temperature.

3. A composition according to claim 1 or 2, wherein said chemical crosslinking agent is selected from polyacids, polyanhydrides and hydrazides which are solid at ambient temperature and insoluble in the monomer or polymer until heated to soldering temperature.

4. A composition according to claim 3, wherein the polyacid is selected from polymers containing two or more carboxyl groups and di- and polycarboxylic acids and di-and polyanhydrides.

5. A composition according to claim 4, wherein the

polycarboxylic acid is a C<sub>8</sub> or greater dicarboxylic acid.

5 6. A composition according to claim 3, wherein the hydrazide is a monohydrazide, dihydrazide or polyfunctional hydrazide.

10 7. A composition according to any one of claims 3 to 6, wherein the crosslinking agent contains a dihydrazide and/or a dicarboxylic acid.

15 8. A composition according to claim 7, wherein the crosslinking agent contains adipic dihydrazide and/or dodecanedioic acid.

9. A composition according to claim 4, wherein the crosslinking agent is a styrene acrylic acid copolymer.

20 10. A composition as claimed in any preceding claim which contains from 30 to 70 parts by weight of thermosetting resin.

25 11. A composition according to any one of claims 1-9, wherein said polymer is an epoxy resin.

12. A composition according to claim 11, wherein said polymer is a B-staged epoxy resin.

30 13. A composition according to claim 12, wherein the said polymer is a diglycidyl ether of bisphenol A.

35 14. A composition according to claim 10, wherein the said resin is a tri- or tetrafunctional epoxide or a difunctional cycloaliphatic epoxide or a mixture of two or more such epoxides.

15. A composition according to any preceding claim,  
which has a thermosetting polymer - solid crosslinking  
agent/flux content in which there are from 30 to 70% by  
weight of thermosetting polymer and from 70 to 30% by  
weight of solid crosslinking agent/flux.

16. A composition according to Claim 15, wherein said  
thermosetting polymer content is from 50 to 60% by  
weight and said solid crosslinking agent/flux content  
is from 50 to 40% by weight of the total amount of  
thermosetting polymer and crosslinking agent/flux.

17. A composition according to any preceding claim,  
which additionally contains an acid flux which is  
liquid at temperatures below 100°C.

18. A composition according to Claim 17, wherein the  
acid flux is liquid at ambient temperature.

19. A composition according to Claim 17 or 18, wherein  
the acid flux is a monocarboxylic acid, preferably  
containing at least 8 carbon atoms.

20. A composition according to Claim 19, wherein the  
acid flux is a versatic acid, capric acid, caprylic  
acid, lauric acid, stearic acid or palmitic acid.

21. A composition according to any one of Claims 17 to  
20, which has a thermosetting polymer-flux content in  
which there are from 30 to 70% by weight of  
thermosetting polymer and from 70 to 30% by weight of  
flux, which flux is, in turn, made up from 80 to 97% by  
weight of said solid crosslinking agent/acid flux and  
from 20 to 3% by weight of said acid flux.

22. A composition according to Claim 21, which has a

thermosetting polymer-flux content in which there are from 50 to 60% by weight of thermosetting polymer and from 50 to 40% by weight of flux, which flux is, in turn, made up from 85 to 95% by weight of said solid crosslinking agent/flux and from 15 to 5% by weight of said acid flux.

23. A composition according to any preceding claim, which additionally contains a latent reaction catalyst selected from tertiary amines and imidazoles and metallic salts.

24. A composition according to Claim 23, wherein the imidazole is phenyl imidazole.

25. A composition according to Claim 23, wherein the tertiary amine is constituted by self catalysing tertiary amine groups substituting the reactive monomer or polymer.

26. A composition according to Claim 25, wherein the reactive monomer is a tertiary amine-substituted trifunctional or tetrafunctional epoxide.

27. A composition according to Claim 23, wherein the metallic salt is tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

28. A composition according to any preceding claim which further comprises a thermally conductive filler.

29. A composition according to Claim 28, wherein said filler reduces thermal expansion of the composition while not effecting substantially the viscosity thereof.

30. A composition according to Claims 28 and 29, wherein the filler is constituted by nominally  $5\mu$  spherical ceramic beads or hollow spheres.

5 31. A composition according to Claim 28, wherein the filler is a ceramic or glass ceramic powder comprising spherical particles with diameters in the range from 0.1 to  $25\mu$ , preferably 1- $15\mu$ .

10 32. A composition according to Claim 28, wherein the filler is a ceramic or glass ceramic powder consisting essentially of monodisperse spherical particles having a single diameter in the range from, 0.1 to  $25\mu$ , preferably 1- $15\mu$ .

15 33. A composition according to Claim 28, wherein the filler is a thermally conductive ceramic powder.

20 34. A composition according to Claim 33, wherein the ceramic powder is selected from  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  / $\text{ZnO}$ , barium sulphate and diamond dust.

25 35. A composition according to Claim 28, wherein the ceramic powder has a low or negative coefficient of thermal expansion.

36. A composition according to Claim 35, wherein the ceramic material is aluminium lithium silicate.

30 37. A method of producing an electronic device which comprises opposing an electrical component having a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations  
35 corresponding to the terminations of the electrical component, with a thermally curable adhesive

composition according to any one of claims 1 to 36  
being applied to a metal surface at one and/or both of  
said electrical component and said substrate, bringing  
the electrical component and substrate into contact at  
elevated temperature and thereby soldering the  
electrical component to the substrate and  
simultaneously achieving encapsulation thereof in  
thermoset polymer produced from said monomer or polymer  
in situ, catalysis of crosslinking of the thermally  
curable adhesive being achieved by metal oxide removed  
from metal surfaces by the fluxing composition and/or  
salts formed by reaction between metal oxide and  
crosslinking agent.

38. A method as claimed in Claim 37, wherein the  
thermally curable adhesive composition is applied to  
one and/or both of the said electrical component and  
said substrate prior to bringing the two together.

39. A method as claimed in Claim 37 or 38, wherein no  
fluxing agent is applied to either said electrical  
component or said substrate prior to application of the  
solder curable adhesive composition.

40. A method as claimed in any one of Claims 37 to 39,  
wherein the thermally curable adhesive composition is  
applied to a die, which is either in wafer form or as  
separate discrete devices.

41. A method as claimed in any one of Claims 37 to 40,  
wherein the thermally curable adhesive composition is  
applied by screen printing, stencil printing,  
dispensing or spinning.

42. A method as claimed in any one of Claims 37 to 41,  
wherein the thermally curable adhesive composition is

applied in B-stageable form and B-staged in situ.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/01236

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G59/18 H01L21/56 B23K35/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 07542 A (KIRSTEN KENNETH J) 27 February 1997 (1997-02-27) page 31, line 36 - page 32, line 30; claims; example 7	1-42
X	WO 97 07541 A (KIRSTEN KENNETH J) 27 February 1997 (1997-02-27) claims	1-42
X	WO 98 08362 A (CRAIG HUGH P) 26 February 1998 (1998-02-26) claims	1-42
X	WO 93 06943 A (TORANAGA TECHNOLOGIES INC) 15 April 1993 (1993-04-15) claims	1-42
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

30 August 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>CHEMICAL ABSTRACTS, vol. 130, no. 21,  24 May 1999 (1999-05-24)  Columbus, Ohio, US;  abstract no. 289696,  JOHNSON, R.W., E.A.: "Reflow-curable  polymer fluxes for flip chip  encapsulation"  XP002113667  abstract  &amp; PROC. - INT. CONF. MULTICHIP MODULES  HIGH DENSITY PACKAG., 1998, pages 41-45,  -----</p>	1-42

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

PCT/GB 99/01236

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 9707541 A	27-02-1997	EP 0870329 A EP 0843894 A WO 9707542 A	14-10-1998 27-05-1998 27-02-1997
WO 9808362 A	26-02-1998	AU 3781797 A EP 0933010 A	06-03-1998 04-08-1999
WO 9306943 A	15-04-1993	US 5376403 A AU 663342 B AU 2767892 A CA 2120523 A EP 0646048 A JP 7502369 T KR 9710170 B MX 9205644 A US 5538789 A US 5830389 A US 5565267 A US 5716663 A US 5853622 A	27-12-1994 05-10-1995 03-05-1993 15-04-1993 05-04-1995 09-03-1995 21-06-1997 31-08-1994 23-07-1996 03-11-1998 15-10-1996 10-02-1998 29-12-1998